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IDENTIFICATION AND PROPERTIES OF MOLECULAR SYSTEMS  
OF POTENTIAL USE IN SOLAR-PUMPED LASERS

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## I. RESEARCH METHODOLOGY

Solar radiation increases the energy content of gases by heating and by electronic excitation of its molecules. The electronically excited molecules may serve as reservoirs of energy that can be used for example to pump lasers. To achieve this the excited molecules or their products must live long enough to constitute an active laser medium, with an inverted level population. This requires identifying suitable molecules to be excited, and isolating the processes that build up the population inversion. Theoretical and computational methods are valuable in these two tasks.[1]

One of the processes which has already been proven in the laboratory is that in which molecules containing C-I bonds are dissociated to produce metastable I atoms.[2] To model the kinetics of this system one must know the rates of competing processes and hence the quantum yields of dissociation products. This need is typical of the ones which our theoretical work has tried to satisfy.

Our approach has used the concepts and computational tools of theoretical chemistry to investigate molecular properties needed in the development of direct solar-pumped lasers.[1] Our efforts have been directed towards: (A) identification of suitable molecules by developing general guidelines; (B) study of the molecular dynamics of dissociation, to calculate cross sections and quantum yields versus radiation wavelength; and (C) calculation of potential energy surfaces and transition dipoles including spin-orbit coupling.

Part (A) could be carried out using qualitative concepts of chemical bonding and spectra, and led to suggestions of new compounds for laboratory studies.[3] Some of these were prepared at the University of Florida [4] and later tested for laser action at the NASA Langley Labs and at the Joint Institute for Laboratory Astrophysics.[5] It was also proposed that a com-

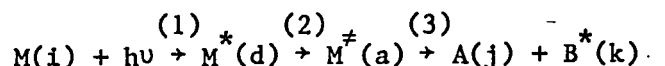
bination of infrared and visible excitation might lead to increased yields of desired products. This was theoretically investigated in Part (B).

Part (B) presented a challenging theoretical problem because computational methods were not available to do the dynamics of electronically excited polyatomic molecules. This problem has been solved by developing an eikonal approximation in which input information from classical mechanics simulation is used to construct wavefunctions and to calculate transition probabilities, or quantum yields of products of dissociation.[6-8]

Part (C) has required a longer time, partly because we felt that its content is sufficiently broad to justify a general treatment that would be useful in other studies. It has been approached with simple one-electron theories of the Huckel type [9,10] and with approximations related to diatomics in molecules.[11] A more fundamental approach, continued at the present time, relies on configuration interaction methods where certain differential overlaps are neglected to decrease the computational time for molecular integrals.[11,12]

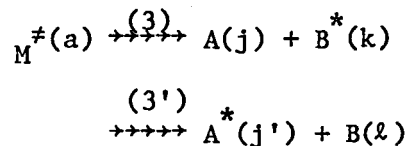
## II. IDENTIFICATION OF SUITABLE MOLECULES AND PROCESSES USING SIMPLE THEORETICAL CONCEPTS

We can describe the photodissociation of a molecule M by photons of frequency  $\nu$  with the following steps:



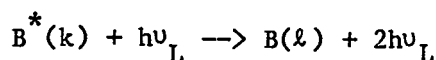
Step (1) leads from the reactant in its initial ground electronic state and vibrational-rotational state i to an absorption "doorway" state d of electronically excited  $M^*$ . These "doorway" states depend on the density of energy levels of  $M^*$  [13]. In step (2) the molecule must rearrange by intramolecular energy transfer into an activated state a from which it will dissociate. The dissociation step (3) must lead to the required metastable product  $B^*$  in a state k,

with sufficiently high probability. Furthermore, in a number of cases (Section III) the activated state may break up into other products, e.g.



with a quantum yield  $\Phi_3$  for the desired products of step (3). These steps can be investigated with the theoretical tools briefly described in Section III.

The laser process is then



where  $\nu_L$  is the laser frequency, and  $B(l)$  is the fragment in its ground electronic state, but possibly in an excited vibrational-rotational level  $l$ .

The criteria used to identify suitable molecules were

- (i) Broad band absorption in the visible, preferably at wavelengths of about 500 nm, where the solar spectrum is most intense.
- (ii) Dissociation into metastable products which can be used as an active laser medium with a narrow emission band.

The ongoing search for suitable molecules has made use of results in the literature [14-16] and of simple chemical concepts such as atomic electronegativities and bond strengths. Promising candidates are halogenated polyatomic molecules of type  $RX$ ,  $R'XY$  and  $R''XY_2$ , where  $R$ ,  $R'$  and  $R''$  are perfluoro alkyl, alkyl or benzyl groups,  $X=I$  and  $Y=Br$ . Diatomic halogen molecules are also possible candidates. To the previous criteria one should add, for molecules with C-I bonds

- (iii) The polyatomic should have a high absorption coefficient for photons of energy equal or larger than the C-I bond energy.
- (iv) The excited polyatomic  $(RC-I)^*$  should have a repulsive potential between C and I, leading to  $RC + I^*$ .

There is some experimental evidence that compounds with two I atoms attached to the same C have much higher absorption coefficients [15]. Also, substitution of a F by Br at a  $\beta$ -carbon (the one next to a C-I bond) appears to increase the absorption. This suggests theoretical studies of  $\text{CF}_2\text{I}_2$  and 1,2- $\text{C}_2\text{F}_4\text{BrI}$ .

These suggestions were based on the observation that hydrocarbons with a C-I bond may enormously increase their absorption coefficient if a H in the  $\alpha$ -Carbon (that bound to I) is replaced by another halide. E.g., at  $\lambda = 308\text{mm}$ , one finds[15]

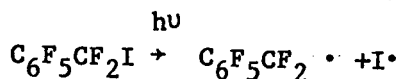
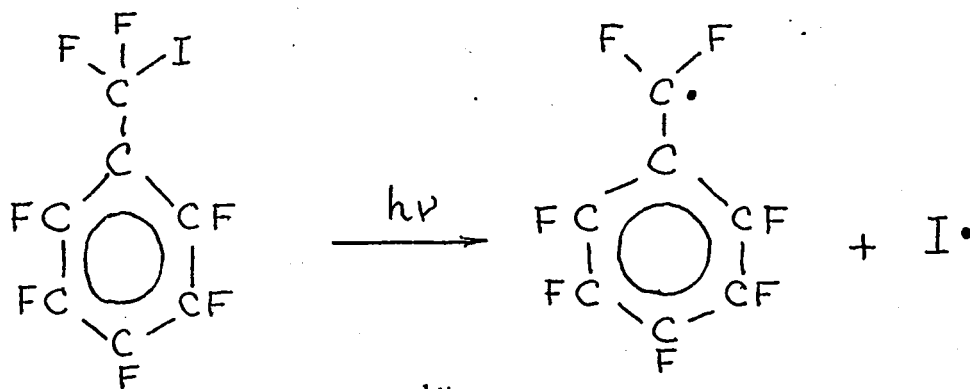
	$\epsilon (\text{L mol}^{-1} \text{cm}^{-1})$	$\phi_{\text{I}}^*$
$\text{CH}_3\text{I}$	2.2	0.05
$\text{CH}_2\text{I}_2$	860	0.25

where  $\epsilon$  = absorption coefficient and  $\phi_{\text{I}}^*$  = quantum yield of  $\text{I}^*$ .

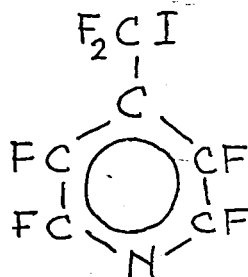
Also, the presence of two C-X bonds, with  $\text{X} = \text{Br}, \text{I}$ , produces much larger transition dipoles and  $\epsilon$ 's. As a result, more energy is absorbed and redistributed, and the C-X bonds break more frequently, with a  $\phi_{\text{X}}$  much larger than twice the old  $\phi_{\text{X}}$  yield. Very recently, additional results have been published on experimental yields of these compounds.[17]

The compound  $\text{CF}_2\text{I}_2$  was prepared [4] and tested [5] as a result of the above suggestions.

Another group of compounds, also suggested [3], is that based on aromatic groups. Consider the following fluorinated compound, and its photodissociation products,



The absorption coefficient should be large because the delocalized electrons in the ring give high transition dipoles; the C-I bond should be weak because R<sup>•</sup> is very stable. Absorption might increase if a C-F group in the ring is replaced by N as shown in the Figure below



This group of compounds has not yet been explored, to our knowledge.

While the above comments refer to the identification of new suitable compounds, one could also search for alternative processes. One such process was proposed [3], based on the dissociation of bonds previously excited by heat or, more conveniently, by tuned infrared radiation.

At high temperatures, C-I bonds may be vibrationally excited and as a result dissociation by visible or UV may increase. This could be investigated by using the same radiation of wavelength  $\lambda$  and increasing the temperature  $T$ . In practice, part of the solar energy would be used as a black body (of high  $T$ ) and part as direct radiation for dissociation. A theoretical study should provide the dissociation rate  $k_{\text{diss}}(v, \lambda)$  where  $v$  = vibrational state of C-I bond.

This alternative process has not yet been explored, to our knowledge.

### III. QUANTUM MOLECULAR DYNAMICS OF PHOTODISSOCIATION

There have been numerous theoretical studies of polyatomic photodissociation. The early work, based on approximate quantum mechanical theories, has been described in two reviews [18,19]. An accurate quantal approach was also presented quite a while ago [20] and has been applied to several systems of

experimental interest.[21] Other developments have introduced a quantized electromagnetic field (i.e. photon scattering) [13] and the electron-field representation.[22] More recent work has dealt with angular momentum coupling and angular distribution of fragments [23,24] and with propagation techniques to solve inhomogeneous differential equations for half-collisions.[25,26] Wavepackets techniques and their semiclassical limit have been used to describe polyatomic photodissociation [27] and work has also been carried out using classical trajectories with Franck-Condon initial distributions in the excited electronic states.[28]

In view of all this work it would appear unnecessary to develop yet another approach to photodissociation. However, many of the best studied molecules involve more than three atoms and several excited potential energy surfaces. To understand their break-up one must follow the dynamics of many degrees of freedom and electronic transitions between potential surfaces. Quantal methods are not practical for this purpose, and would generate more information than is usually wanted at great expense in computing time. At the other end are classical methods with which one can easily follow several atoms but that have several shortcomings. They must introduce a distribution of initial conditions for motion on the excited potential surfaces, which does not allow for the proper phase interference of the initial and final states, and they can identify initial and final quantum numbers only in an average sense.

Our work under this Grant has provided a method by which, starting with classical trajectories and their coupling to electronic transitions, one can obtain state-to-state transition amplitudes even for polyatomics with more than three atoms. This can be done with the selfconsistent eikonal method we have recently described.[6] It is based on the simultaneous integration of the Hamilton equations for the nuclear motions and of time dependent equations for electronic amplitudes. It is related to methods previously developed to



describe atom-atom and heavy-particle collisions.[29-31] The generated information on trajectories and mechanical action functions can be used to construct eikonal wavefunctions and to calculate their integrals as they appear in the transition amplitudes of scattering theory. This method has been applied to a simple model of break-up of the C-I bond to show how the equations describe the transition from the ground electronic potential to the excited one,[7] and to electron transfer in ion-diatom collisions to compare with other work.[32] It provides branching ratios when more than one excited surface is involved, without requiring any additional assumptions on transitions between surfaces. It has the further advantage of being applicable to cases where there may be rearrangement after photon absorption, leading to e.g. A+X and B+Y products. In this case it is necessary to also describe the rearrangement A+X  $\rightleftharpoons$  B+Y in the excited electronic state. This is a situation which so far can be treated quantum mechanically only for collinear triatomics or specially simple systems, but that can be readily treated with eikonal approximations.

A general treatment of molecular photodissociation may best be done by quantizing the electromagnetic field and considering the absorptive scattering of photons by the molecule [33]. Quantum yields (or photon scattering cross sections) may be obtained by solving the stationary Schrödinger equation

$$H\Psi = E\Psi$$

$$H = K_n + H_{el} + H_f + H_{mf}$$

where  $\Psi$  is the molecule-field state of total energy  $E$ , and the hamiltonian  $H$  has been decomposed into the nuclear kinetic energy operator  $K_n$  and the energy operator terms  $H_{el}$ ,  $H_f$  and  $H_{mf}$  for the electrons, the field and the molecule-field interaction respectively. The latter can be written, for the low fluxes of solar radiation as

$$H_{mf} = -\vec{E} \cdot \vec{D}$$

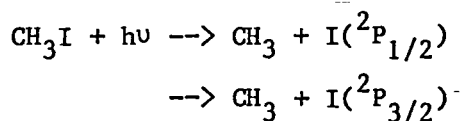
where  $\vec{E}$  is the quantized electric field and  $\vec{D}$  is the operator of the molecular electric dipole.

The selfconsistent eikonal approximation is valid for short de Broglie wavelengths of the nuclear motion. The wavefunction for nuclear motions on the potential energy surface corresponding to the electronic state  $\Gamma$  is written in the form

$$\Psi_{\Gamma}(Q;p) = \chi_{\Gamma}(Q;p)\exp[iS(Q;p)/\hbar]$$

where  $Q$  is the set of nuclear coordinates,  $p$  is the relative momentum of the dissociating fragments,  $S$  is the eikonal function and  $\chi$  is a preexponential function. Then  $S$  is calculated with the Hamilton equations and  $\chi$  by solving the equivalent to the time-dependent Schrodinger equation. These equations are coupled and solved simultaneously. How this is done is described in detail in reference [8]. Once the eikonal wavefunction is known, one can replace it in the expression for the quantal transition amplitude  $T$  to obtain state-to-state cross sections for dissociation and to find from these, quantum yields.

The validity of the approximation and the computer codes have been checked by carrying out calculations for the photodissociation



where  $\text{CH}_3\text{I}$  and  $\text{CH}_3$  are in their ground electronic states, and  $\text{CH}_3$  is in any of its vibrational levels  $v$ . The calculations were done for coupled potential energy surfaces leading to the two product channels, provided to us together with exact quantal results which we could compare with [34]. The comparison is shown in Figures 1 and 2. One finds satisfactory agreement in the dependence of transition probabilities with the  $v$  quantum number, for each radiation wave-

length, in this case  $\lambda = 266$  nm and 248 nm. Quantum yields could be obtained and are shown in Table 1, together with other results from experiment and theory.

Table 1. Quantum yields from the cross sections quotients  $\sigma(I^*)/\sigma(I^*+I)$

Source	$\lambda = 266$ nm	$\lambda = 248$ nm
Present work	0.82	0.77
Other theory[34]	0.87	0.86
Experiment	$0.78 \pm 0.11^a$	$0.81 \pm 0.03^b$
Experiment		$0.58^c$

a) Riley and Wilson, Disc. Faraday Soc. 53, 132 (1972)

b) Baughcum and Leone, J. Chem. Phys. 72, 6531 (1980)

c) Hunter and Kristjansson, Chem. Phys. Lett. 58, 291 (1978)

One finds good agreement, and confirmation of the well known fact that the excited atom is produced with higher yield.

Our approach is being continued at present [35], with calculations of isotope variants and effects of anharmonicity, as well as of dissociation of  $CF_3I$ . While this can now be readily done, the most important contributions of the selfconsistent eikonal approach should be to the description of larger molecules, for which other methods are not suitable.

Furthermore, since our calculations can provide distributions of products versus the initial vibrational states, we could investigate whether quantum yields could be increased by vibrational excitation of reactants concurrently with absorption of visible or UV radiation. This possibility, mentioned in Section II, could lead to more efficient lasers, but is not being pursued at the present time.

#### IV. POTENTIAL ENERGY SURFACES AND TRANSITION DIPOLES

Our studies of the photodissociation dynamics have disclosed the need for values of several electronic structure properties. For molecules of type  $R_3CI$ , it is necessary to know the repulsive potential energy surfaces leading to  $R_3C + I^*, I$  as functions of the R-C-R angle. That is, surfaces must be obtained in the two-dimensional space of C-I and R-C-R variables. For molecules of type  $R_2CXY$  the immediate need is for surfaces versus the C-X and C-Y distances (this includes  $CF_2I_2$ ). Transition dipoles must be known not only in magnitude but also in the direction of breaking bonds as functions of the above distances.

Our work on electronic structure has focused on two aspects. Presently available non-relativistic INDO-CI programs (to do Configuration Interaction calculations with Incomplete Neglect of Differential Overlap) have been used to investigate the importance of single and double excitations, which must be included to dissociate to the proper fragments with the correct asymptotic transition dipoles. However, most of the work in this area has concentrated on how to incorporate the spin-orbit coupling in the calculations.

Based on our earlier literature investigation and preliminary calculations we concluded that spin-orbit effects play such a dominating role in the description of C-I bond breaking that we could not expect to get reliable predictions with the usual perturbational approach but should consider the electrostatic and spin-orbit effects simultaneously.

After careful consideration of the quality of results we can expect with various approaches, the computational resources needed for those approaches, and the length of time it would take to develop them, we decided upon the following.

To begin with we wanted to determine to which extent one could obtain potential energy differences using simple approximations of the Huckel type, which provide one-electron energies, but extended to include spin-orbit

coupling. There have been two treatments in the literature on this, one adding the spin-orbit coupling to the non-relativistic hamiltonian [9], and the other starting with a relativistic one-electron hamiltonian [10].

We have performed calculations with a program (Quantum Chemistry Program Exchange ser. 468 (1983) named REX, based on the second approach but slightly modified [36] to improve efficiency. Results for  $\text{CH}_3\text{I}$  are shown in Figures 3 and 4. The full lines in Fig. 3 refer to the present calculations and the dashed lines to the semi-empirical potentials [34]. The full lines have been shifted down for clarity, but should go to the same limit of large distances  $\text{H}_3\text{CI}$  between I and the center of mass of  $\text{CH}_3$ . Here the distance from C to the plane  $X = \text{H}_3$  of the hydrogens is  $R_{\text{CX}} = 0.75$ . Figure 4 shows a cut of the calculated surfaces for a fixed  $R_{\text{CI}}$  distance.

These surfaces are qualitatively correct and could perhaps be used to compare the interaction potentials of series of compounds, but to be more quantitative in the calculation of quantum yields it appears necessary to include electron selfconsistency and correlation in the electronic structure calculations. Also, it would be convenient to calculate the Born-Oppenheimer or momentum couplings between the surfaces, to account for their crossings in a diabatic picture of dissociation [37]. These crossings appear in the semi-empirical potentials of Fig. 3, and are likely to also appear in other systems.

We could fairly quickly have programmed the spin-orbit coupling on the level of the Hartree-Fock method but, as the Hartree-Fock level rarely is adequate in the description of bond breaking and excited states and since it is not feasible to use it as basis for the needed correlated calculation, such an effort would be of limited utility in the long run.

Instead we decided to make a non-relativistic Hartree-Fock calculation and use the resulting orbitals to generate a basis of configurations in which we expand the wavefunction, i.e. for the CI calculation. These expansion coef-

ficients, the CI coefficients, are then determined using the complete Hamiltonian, including the spin-orbit coupling.

We believe this approach is the simplest both computationally and in its implementation. Furthermore this approach has the advantage of easy interpretation.

After having completed the formal development of the theory we are now programming the approach we decided upon.

The computational strategy is as follows:

- (1) Find the equilibrium geometry for the molecular electronic ground state.

This step is recommended even for molecules where the geometry is known, since the semiempirical INDO-CI scheme needs fine tuning.

- (2) Do the same calculations with spin-orbit coupling included. This should not produce any substantial change in the ground state geometry, but should be checked.

- (3) Do a spectroscopic INDO-CI calculation at the equilibrium geometry.

Look for large transition moments for transitions within the solar spectrum.

- (4) Calculate the ground state and the appropriate excited state potential energy surface, or parts thereof including pertinent bond breaking.

- (5) Feed the energies and the dipole transition moment as a function of geometry into the dynamical program discussed in Section III.

This strategy is being pursued at present, with the programming of the matrix elements of the spin-orbit coupling between the configurations included in the CI procedure [38].

## V. CONCLUSIONS

Our contributions to the identification of molecular compounds suitable for solar pumped lasers have been based on the use of simple theoretical concepts,

on the development of a new approach to molecular dynamics, and on the consideration of potential energy surfaces and transition dipoles for compounds where spin-orbit coupling is important.

Simple theoretical concepts helped us identify compounds of the type  $RR'CXY$ , with R and R' organic groups, and X and Y halide atoms, as likely candidates because of their highly enhanced absorption coefficients over compounds with a single halide atom. Some of these compounds have been experimentally studied both at NASA and at other laboratories. Some other compounds of that type, where R is an aromatic group such as a benzyl derivative, would appear to also hold some promise, but they have not yet been considered, to our knowledge.

Recent developments on multiphoton dissociation have suggested that a combination of vibrational excitation followed by electronic excitation, that is the use of both infrared and visible or UV radiation, could lead to enhancement of the desired quantum yields at certain wavelengths. We have pointed out this possibility, and have done some theoretical calculations of the related yields, as functions of the initial vibrational state of selected compounds, to make sure that our molecular dynamics approach can describe such processes. This is the case, so that the codes as presently developed could be used to deal with this possibility if additional work was desired.

The dissociation dynamics of the compounds of interest has been treated with a newly developed approach, a selfconsistent eikonal approximation to state-to-state transitions, that can include transitions among potential energy surfaces and can provide results for polyatomics. It has been tested for  $CH_3I$  and has turned out to be very useful for other problems involving electronic energy and charge transfer. Work remains to be done in this area to treat large polyatomics. For these it is convenient to extend the theory to account for stochastic forces exerted by the environment on the portion of the molecule excited by the radiation. Without this extension the present approach could be

used but would involve long computational times.

The theoretical tools required to calculate potential energy surfaces and transition dipoles have been considered, and a determination has been made of the best way to approach the problem, which is complicated by the important effect of spin-orbit coupling in compounds of iodine. The proposed approach is based on the generation of eigenstates of the non-relativistic Hamiltonian followed by incorporation of the spin-orbit coupling by configuration interaction. This is a substantial effort which is yet in progress with other support. Within the period of this work it was possible to carry out simpler one-electron calculations based on the relativistic Huckel approximation, which includes spin-orbit coupling but not electronic interactions. Even so, this could be useful in further work when comparing series of compounds.



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## VII. PUBLICATION AND CONFERENCE PRESENTATIONS

### A. Publications

1. David A. Micha, "A Self-Consistent Eikonal Treatment of Electronic Transitions in Molecular Collisions," J. Chem. Phys. 78, 7138-45 (1983).
2. P. K. Swaminathan and David A. Micha, "A Self-Consistent Eikonal Treatment of Photodissociation by Visible Radiation," Int. J. Quantum Chem. S16, 377-90 (1982).
3. David A. Micha and P. K. Swaminathan, "Photodissociation of Polyatomics by Visible and U.V. Radiation: The Selfconsistent Eikonal Approximation," QTP Report 766, (1984), to be published.
4. W.D. Edwards, Y. Öhrn, B.L. Weiner and M.C. Zerner, "Semiempirical Antisymmetrical Geminal Power Calculations for Molecular Spectra," Int. J. Quantum Chem. Symp. 18, 507 (1984).

### B. Unpublished report

1. John Bellum and D. A. Micha, Quantum Theory Project, University of Florida Report "A survey of fundamentals in the theory of photon-molecule interactions," Oct. 1981, submitted to NASA.

### C. Conference presentations

1. P. K. Swaminathan and D. A. Micha "A Semiclassical Treatment of Molecular Dissociation by Visible Radiation", International Symposium on the Quantum Theory of Matter, Palm Coast, Florida, March 7-13, 1982.
2. D. A. Micha "Theory of Molecular Photodissociation", Department of Chemistry, University of California, Santa Barbara, Oct. 29, 1982.
3. D. A. Micha "Photodissociation of Molecules by Visible and UV Radiation", Department of Chemistry, University of Florida, Gainesville, Nov. 16, 1982.
4. D. A. Micha and P. K. Swaminathan "Molecular Photodissociation by Visible and UV Radiation: Time-Evolution and State-to-State Cross Sections", Bates International Symposium, Palm Coast, Florida, March 3-5, 1983.
5. J. A. Olson, P. K. Swaminathan and D. A. Micha "Self-Consistent Eikonal Treatment of Molecular Photodissociation and Diabatic Rearrangement", American Physical Society March Meeting, Los Angeles, California, March 21-25, 1983.
6. P. K. Swaminathan and D. A. Micha "Molecular Photodissociation by Visible and UV Radiation: State-to-State Cross Sections from Eikonal Distorted Waves", XIV Southeast Theoretical Chemistry Conference, Tallahassee, Florida, June 21, 1983.
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8. P. K. Swaminathan and D. A. Micha "State-to-State Cross Section for Photodissociation of Polyatomic Molecules by Visible and UV Radiation", International Symposium, Palm Coast, March 5-10, 1984.
9. C. D. Stodden and D. A. Micha, "Quantum Yields for Photodissociation of Polyatomic Molecules by Visible and UV Radiation", "Sanibel Symposia", Marineland, Florida, March 18-23, 1985.

# FIGURE CAPTIONS

- Fig. 1 Cross sections for the photodissociation of  $\text{CH}_3\text{I}$  leading to  $\text{I}^*(^2\text{P}_{1/2})$  (full circles) and to  $\text{I}(^2\text{P}_{3/2})$  (open circles) for radiation of wavelength  $\lambda=248$  nm. Shown versus the vibrational quantum number  $v$  of the fragment  $\text{CH}_3$  umbrella mode. The full lines are our present results, the dashed lines are from Ref. (34).
- Fig. 2 Same as Figure 1, but for  $\lambda=266$  nm.
- Fig. 3 Ground-state and excited-state potential energy surfaces for  $\text{CH}_3\text{I}$  versus the distance  $R_{\text{CI}}$  from I to the center of mass of  $\text{CH}_3$ , for a fixed distance  $R_{\text{CX}}=0.75$  between C and the plane of  $(\text{H})_3=\text{X}$ . The dashed lines are calculated with parameters fixed by experiment [34]. The full lines are relativistic extended Hückel calculations performed by us, that include spin orbit coupling. The latter lines have been shifted down to clarify the figure; the potential energies at large  $R_{\text{CI}}$  go to  $\text{I}(^2\text{P}_{3/2})$  and  $\text{I}^*(^2\text{P}_{1/2})$ .
- Fig. 4 Potential surfaces from the relativistic extended Hückel calculations for fixed  $R_{\text{CI}}$ , versus  $R_{\text{CX}}$ .

FIGURE 1

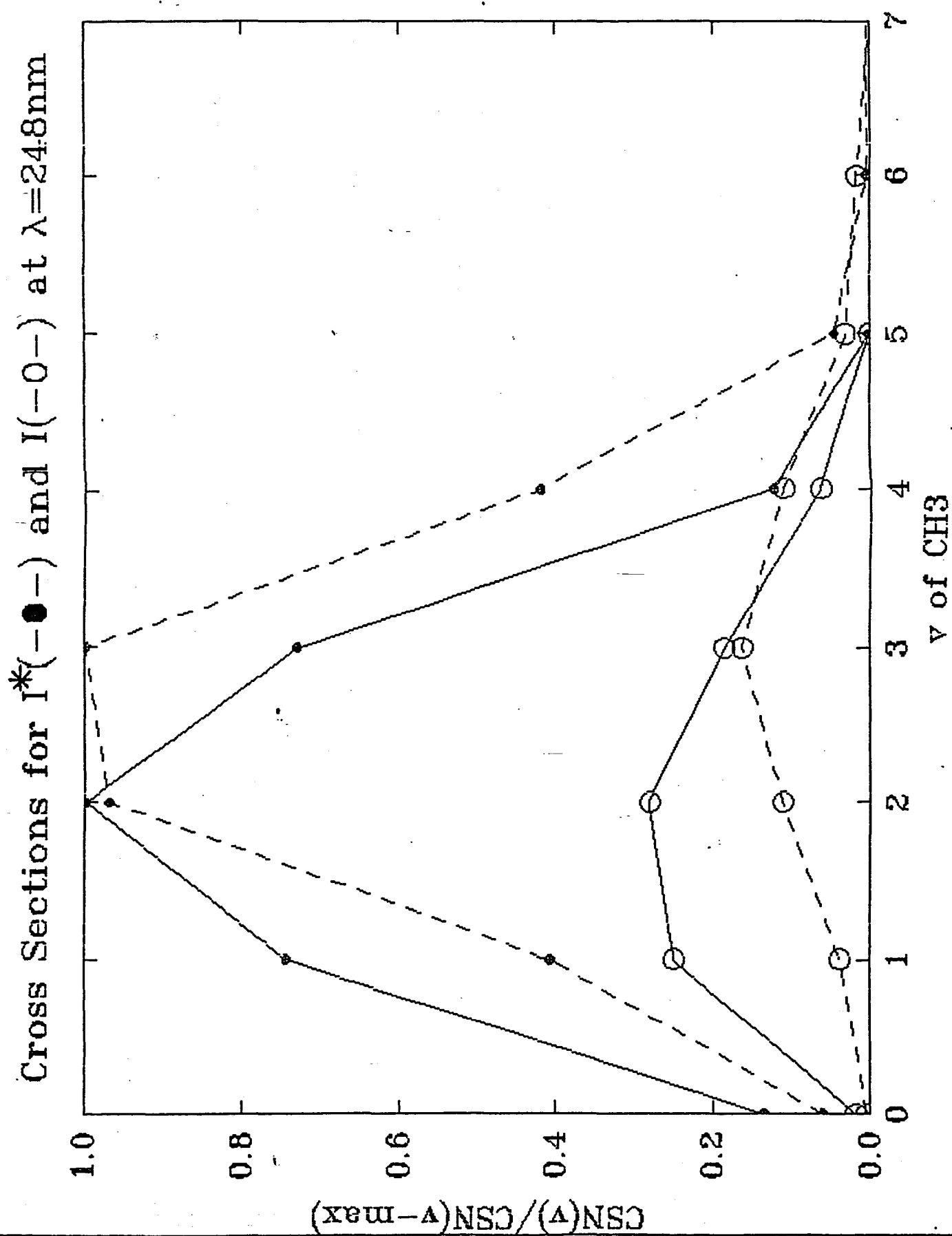
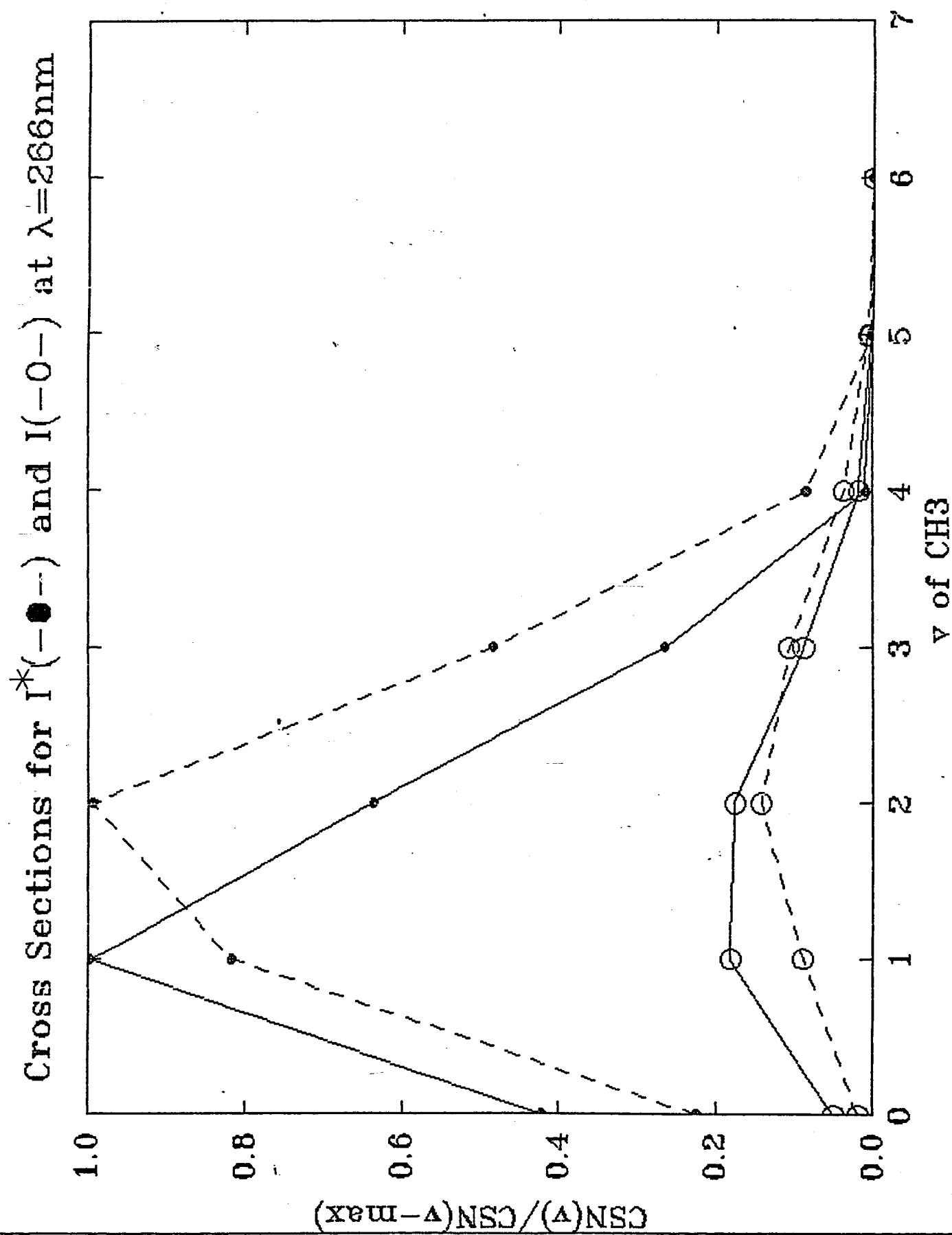


FIGURE 2



# CH3I POTENTIAL(from REX)

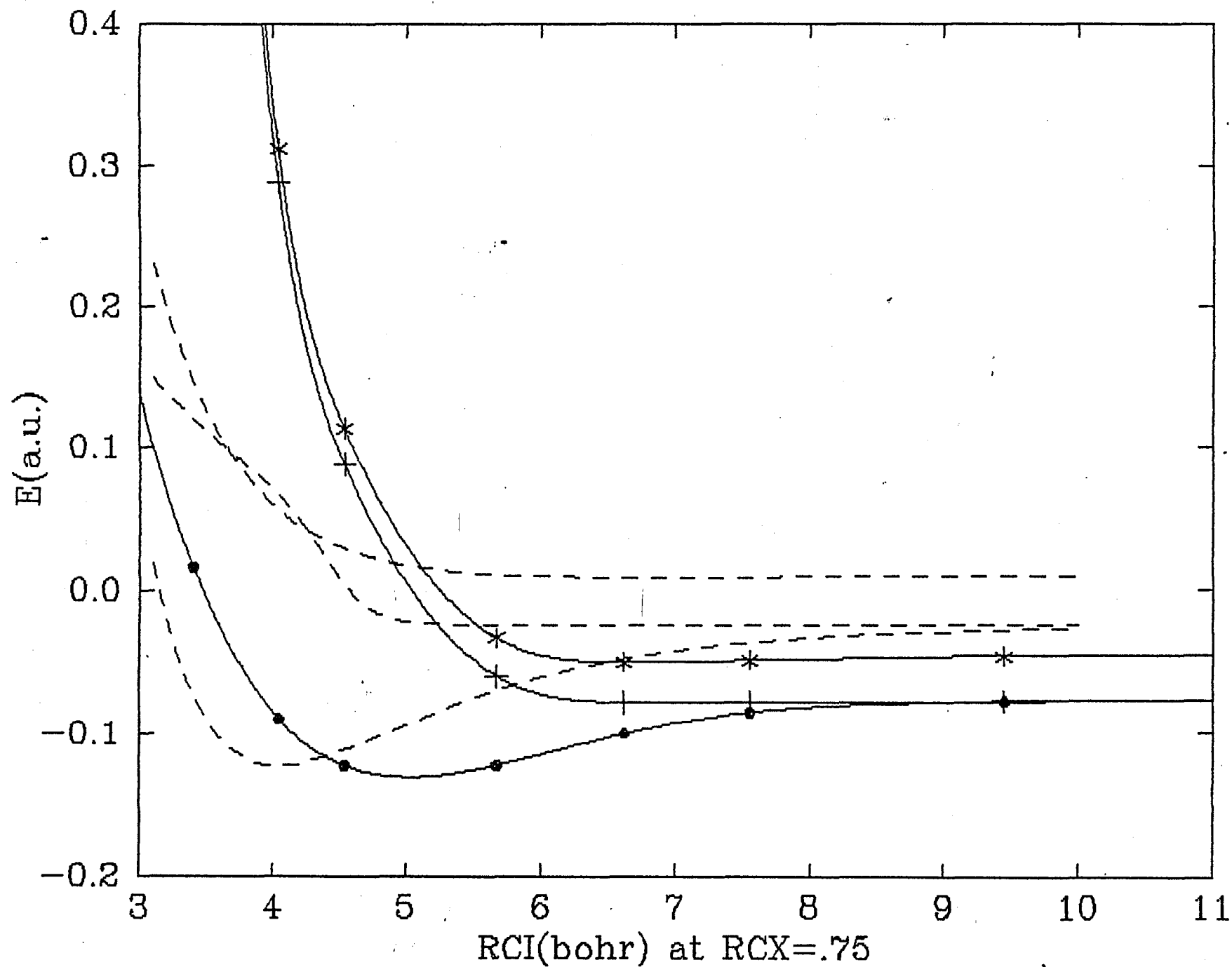


FIGURE 3



# CH3I POTENTIAL(from REX)

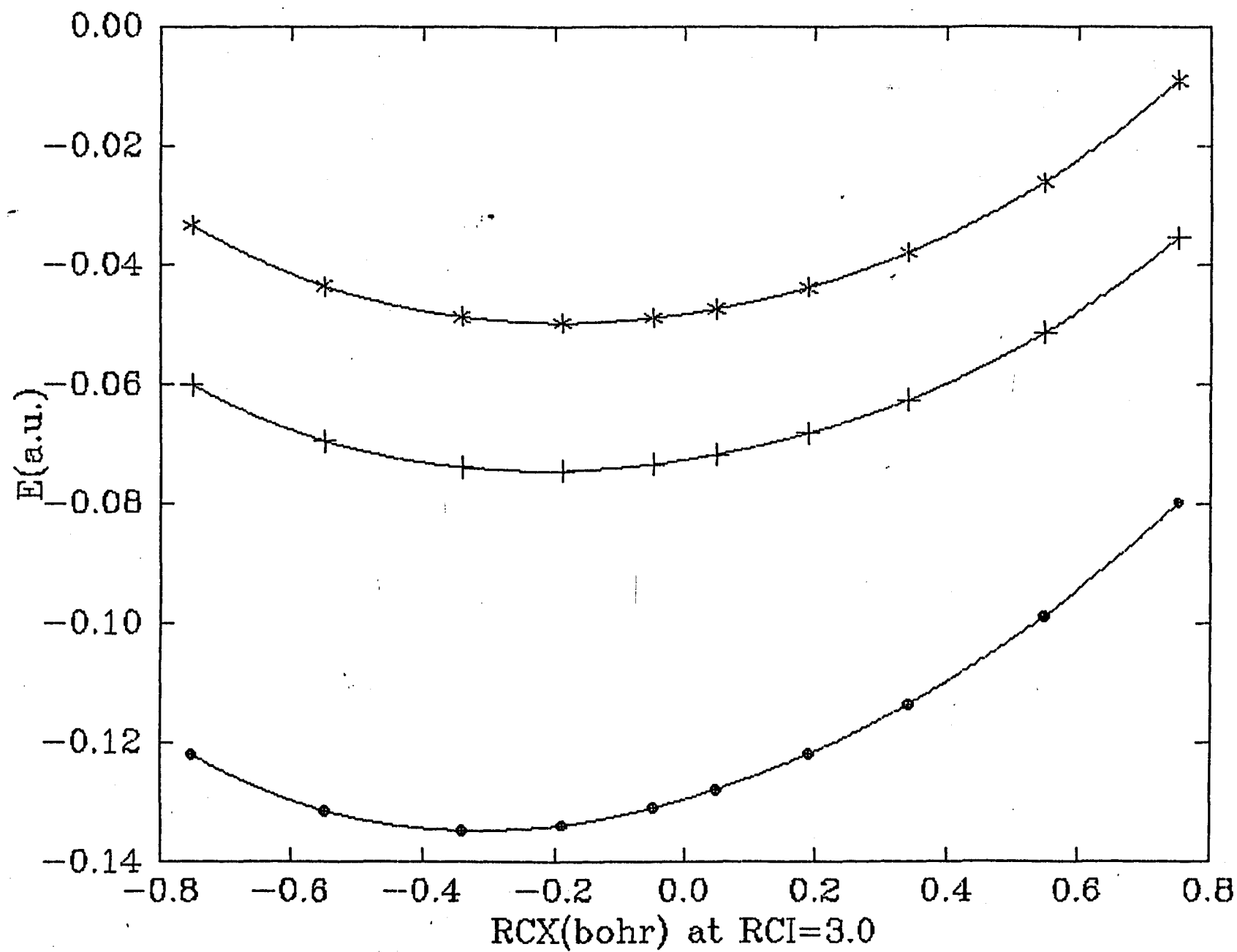


FIGURE 4

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